Reaction and alteration of mudstone with cement pore fluids

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The construction of a repository for geological disposal of nuclear waste will include the use of cement-based materials. Following closure, groundwater will saturate the repository and the use of cement will result in the development of a highly alkaline porewater, pH >12.5 in the case of Ordinary Portland cement (OPC). The alkaline fluid will migrate and react with the host rock, affecting the long-term performance of the repository altering the physical and chemical properties, including radionuclide behaviour. Understanding these changes forms the basis for modelling the long-term evolution of the repository. This study focused on the alteration due to OPC-type leachates on mudstone, a potential candidate host rock in Japan. It was anticipated that firstly, clay minerals would react with the high pH fluids and that silicate minerals would provide longer term buffering; this study was aimed at determining the specific nature and extent of these reactions.

A series of batch (to provide long-term equilibrium data) and flow experiments (to provide spatial and temporal data) were conducted inside a N_2 atmosphere glove box, with Horonobe mudstone, and simplified OPC leachates. These represented a ‘young’, with high pH and high levels of Na and K, and a later, ‘evolved’ leachate (portlandite saturated) corresponding to the early stages (100’s to 10,000’s y) in the evolution of cement porewater. Fluid analysis was by Inductively Coupled Plasma Mass Spectrometry and Ion Chromatography, and determination of pH, and E_h. Solids were examined by scanning electron microscopy (SEM).

Batch experiments were conducted at durations of up to 56 days, at lab temperature, ≈25˚C. The pH of the reacted fluids decreased compared to the initial values, pH≈13.4 to 8.5 and pH≈12.5 to 7, for the ‘young’ and ‘evolved’ fluids respectively. This was reflected in the fluid chemistry with large decreases in [K] observed, compared to the ‘young’ fluid. In the ‘evolved’ fluid experiments, [Ca] decreased and [Na] increased over time. Si showed initial gains, consistent with clay/silicate dissolution, which then decreased over time. The changes in Ca and Si were reflected in the observation of secondary CSH phases with differing Ca:Si ratios. Changes in cations may be due to ion exchange with the clay minerals present. This behaviour is consistent with reaction of the clay minerals, though evidence for this from mineralogical analysis of reacted solids was inconclusive, due to the nature of the mudstone.

Flow experiments using packed columns, were conducted using the ‘young’ fluid, at ≈25˚C, flow rates ≈0.5 ml/h. Si levels showed an initial increase then a reduction, whereas [Ca] dropped immediately to around half value of the starting fluid and then remained constant. Na levels remained close to the ‘young’ fluid throughout, but K showed an initial decrease followed be a recovery to close to the initial levels, this may reflect early ion exchange reactions with sites becoming occupied over the first 400 h of flow. As with the batch experiments, the changes in Ca and Si were due to the formation of secondary CSH phases. Examination of the saturation indices (SI) of selected minerals for the reacted fluids showed CSH to be saturated, and clay minerals to be under saturated suggesting continued dissolution.

In all experiments, S levels increased and although the Horonobe mudstone contains minor pyrite, oxidation of which was the likely source of the S, no attempt was made to control redox so this may simply reflect the initial oxidising experimental conditions.

In summary, the reaction of the mudstone with OPC type fluids demonstrated that long term, its chemical buffering capacity, leading to a reduction in the pH of the leached fluid, dissolution of primary minerals and subsequent precipitation of CSH phases with differing Ca:Si. This behaviour is consistent with previous similar studies, with Ca and Si concentrations being controlled by CSH phase precipitation.

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